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THE FORMATION OF ACIDIC TRACE ORGANIC BY-PRODUCTS FROM THE CHLORINATION OF HUMIC ACIDS

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16. ABSTRACT

A method for concentrating and analyzing acidic trace organics produced by the chlorination of humic acids at concentrations approximating common drinking water levels is described. Data are compared from several humic acid sources.

Specific compound analyses of the extracts were conducted by fused silica capillary column gas chromatography/mass spectrometry. Mass spectral and chromatographic retention data were used to characterize the compounds. Few differences were found in the types of compounds formed from the chlorination of humic acids from the different sources. A notable difference from other published work was the tentative identification of ring-chlorinated methoxy or phenolic aromatic acids.

A granular activated carbon concentration column gave better recoveries of a wide range of compounds than an XAD-8 resin column, but some higher molecular weight compounds, particularly aromatics, were recovered more efficiently from the XAD-8 column.

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INTRODUCTION

The discovery that trihalomethanes (THMs) were formed in drinking water during chlorination for disinfection,[1,2] follow-up studies demonstrating the ubiquitous occurrence of THMs in chlorinated water,[3,4] and the extrapolation of results from animal studies[5] to suggest that ingestion of THMs posed a risk to human health led to the promulgation of federal regulations in 1979 limiting the concentration of total THMs in drinking water to 0.10 mg/L.[6] Concurrent research indicating that naturally occurring humic substances were likely precursors to THM formation[1,7,8] has led to studies investigating other possible by-products from the chlorination of water containing humic materials.

In chlorinated drinking waters, THMs have been found to account for only 22% to 67% (depending on the source water) of total organic halogen (TOX),[9] and, in studies using a concentrated solution of an isolated aquatic fulvic acid, trichloroacetic acid was the major chlorination product, accounting for 32.1% of the final TOX compared to 17.3% for chloroform.[10] Other studies by Norwood, et. al.[11] and Colclough, et. al.[12] have identified numerous individual by-products from the treatment of concentrated solutions of aquatic humic and fulvic acids with chlorine and chlorine dioxide respectively.

The work described in this chapter attempts to examine the by-products resulting from the chlorination of humic substances at concentrations likely to be found in drinking water applications with the following goals in mind: (1) to develop methodologies suitable for isolating and identifying specific compounds from large volumes of water; (2) to qualitatively and quantitatively compare compounds found in chlorinated humic acid solutions to the corresponding nonchlorinated solutions; (3) to qualitatively

and quantitatively compare compounds formed from the chlorination of humic substances from different sources; and (4) to qualitatively compare the results of chlorinating humic acids at low concentration to that of others using highly concentrated humic acid solutions.

EXPERIMENTAL

Humic substances from four different sources were used: two were humic acids from commercial suppliers, Aldrich Chemical Co. and Fluka Chemical Corp.; a third was an aquatic humic acid isolated from Black Lake, North Carolina, by others,[12] and the fourth was an unconcentrated highly colored lake water from southern Florida that is used as a drinking water source. The humic acid solutions from the first three sources were prepared by dissolving the solid material in a basic solution, neutralizing with acid, buffering with phosphate to pH 7, filtering, and diluting to 40 L to yield a solution of 5-6 mg/L total organic carbon (TOC). The Florida lake water (28 mg/L TOC) was only buffered for pH control. The samples were then split into two 20 L portions; one was chlorinated to 20 mg/L, and the other was maintained as an unchlorinated control. The Florida lake water required a larger chlorine dose (40 mg/L) to maintain a free residual, presumably to satisfy the chlorine demand of its higher initial TOC. After three days at ambient temperature, each chlorinated sample was checked to assure that a free chlorine residual remained and was then dechlorinated with sodium sulfite. Both the chlorinated sample and the control were acidified to pH 2 to prepare for the adsorption step. Ten-to-twenty liters of each of the samples were pumped at approximately 8 ml/min through separate 1.3 cm glass columns containing 25 cm of XAD-8 resin.

The organics were desorbed from the resin by a continuous flow of ethyl ether condensate for 3 hours. This was accomplished by attaching a

side-arm to the adsorption column which allowed vapors from 75 mL of peroxide-free ethyl ether in a heated collection flask connected to the base of the column to pass to a condenser at the top of the column. The condensed ether then drained through the adsorption media and returned to the collection flask. The aqueous layer (from residual water on the resin column) was further acidified to pH 1, separated from the ether layer, and extracted with an additional 25 mL of ethyl ether. The combined ethyl ether fractions were dried with sodium sulfate and concentrated to 5 mL using Kuderna-Danish equipment. The samples were methylated with diazomethane gas following the procedure described by Schlenk and Gellerman,[13] with 5% methanol added to aid methylation and to minimize precipitation in the sample, and held at room temperature for at least 16 hrs. The samples were remethylated by the same procedure just prior to analysis because the yellow color of the extracts prevented visual examination for the presence of diazomethane.

An internal standard, 1-chlorododecane, was added to a 0.1 mL aliquot of the sample just prior to analysis by splitless injection onto a 50 m x 0.20 mm ID fused silica capillary column coated with a methyl silicone fluid. A Finnigan model 9500 gas chromatograph was used with the column exiting directly into the ion source of a Finnigan model 3300 quadrupole mass spectrometer operated at 70 eV in the electron impact mode. The data were collected and processed using the Finnigan INCOS model 2300 data system.

The identification and integration of the individual chromatographic peaks were greatly facilitated by the ability to automate the peak searching and quantitation procedures on the INCOS data system. The first set of samples, however, required extensive interaction by the analyst. First, the mass spectra of all chromatographic peaks, with background subtracted,

were compared to the libraries of 38,728 spectra from the EPA/NIH Mass Spectral Data Base and of 105 spectra which have been identified by researchers at the University of North Carolina from their work with the products of humic acid chlorination using a gas chromatograph/mass spectrometer (GC/MS) capable of accurate mass measurements.[14] If the analyst concluded that a library spectrum matched that of the sample peak, it was entered into a special sample library with its identity, mass fragment intensities, retention time relative to the internal standard, and a principal fragment ion for future quantitation purposes. If the analyst concluded that the sample peak spectrum was valid (i.e., that it was not overly influenced by background or other interferring peaks) but that it did not match any library spectra, it was entered into the sample library as a numbered unknown, again including mass fragment intensities, relative retention time (RRT), and a principal fragment ion.

In subsequent samples, much of the analyst's interaction was eliminated by using the automated procedures of the data system to find and integrate the peak areas of compounds that had been entered into the sample library from previous samples. These procedures used retention time and spectral data from each sample library entry to search for that compound in the new sample file. If a matching peak was found, the area of the principal ion from the library entry was integrated and reported with the compound name from the sample library. To find and identify peaks that had not been previously entered into the sample library, a modified Biemann-Biller peak finding algorithm[15] was used to list peaks that had not matched any of the sample library entries. These peaks were then examined by the analyst and added to the sample library either with identities obtained from the standard libraries or as unknowns.

RESULTS AND DISCUSSION

Because few of the named compounds in this work have been confirmed by the analysis of authentic standards or by any means other than electron impact MS, all identifications listed in this paper are considered tentative unless specifically noted otherwise. Also, in many cases, a library match or specific interpretation could not be made, but the spectra exhibitied unique characteristics, such as clusters of fragment ion peaks or repetitive ion peak patterns. These characteristics allowed the analyst to classify the spectra with other similar compounds. For example, several compounds characterized as "aliphatic acid, methyl ester" in the sample library exhibited the characteristicly strong fragment ions at m/z 74 and 87, but weak responses in the higher mass range precluded any further identification or molecular weight assignment. For other compounds that were characterized only as chlorine containing compounds, clusters of ions resulting from the natural isotopic ratio of ^{35}Cl to ^{37}Cl were observed, but further characterization based on library matches or spectral interpretation could not be made. Characterization of compounds in this way provided a useful tool to monitor the classes of compounds found in the different sample runs. Because capillary column retention time as well as spectral matching was used, a level of confidence was added in determining the recurrence of individual compounds in succeeding samples, even when compounds of nearly identical spectra, such as isomers or members of a homologous series, were present.

The computer reconstructed total ion chromatograms of nonchlorinated and nonchlorinated Fluka humic acid (Figure 1) visually illustrate the

increases in both the numbers and intensities of the peaks produced by chlorination. The largest peak in each chromatogram is the added internal standard which was approximately equivalent to a concentration of 10 ug/L in the original humic acid solutions.

Four broad groups of compounds are shown in Table 1, and the individual peaks that have been tentatively identified or characterized are listed within these groups with a numerical value corresponding to area counts of the peak rounded to the nearest one thousand after normalization on the internal standard. Because response factors were not calculated from known standards, the intensities cannot be related directly to concentration, and the intensity numbers can only be compared with other intensity numbers for the same compound, i.e., within horizontal rows of the table. Even then, the large quantitative variability (discussed below) must be considered. Table 2 lists the unknowns that were found in more than one of the chlorinated humic samples. They have been characterized only as to whether or not they contain chlorine and have been separated into two groups on that basis.

The mono- and dibasic aliphatic acids, mon- and polycarboxylic aromatic acids, and various chloroaliphatic acids listed in Table I generally agree with compounds identified by other investigators where the reaction conditions were more harsh.[10,11,12] Ring-chlorinated aromatic acids, however, were not reported in those studies using similar substrates. One explanation is that the ring-chlorinated aromatic acids may survive intact at the relatively low concentration of chlorine and carbonaceous substrates used in this work but that the aromatic ring structures are further oxidized, or other mechanisms prevail, at the higher concentrations used by other

researchers. Conversely, another explanation may be that the extraction and concentration methodologies used in this study selectively enhanced the concentration of the ring-chlorinated aromatic acids relative to the other chlorination by-products.

Chlorophenols[16] and chloromethoxybenzenes[17] have been reported in chlorinated humic acid samples and highly chlorinated reservoir water, respectively, and 2-chlorobenzoic acid, methyl ester, has been reported, tentatively identified by GC retention time only, by one investigator.[18] These are the only previously reported specific identifications of ring-halogenated compounds resulting from the chlorine treatment of humic materials. Super chlorination of municipal waste waters[19] and pulp bleaching operations[20,21] also yield some ring-chlorinated compounds, and aqueous chlorination of simple phenols to form odorous ring-chlorinated derivatives is also well known in the drinking water industry. The work described in this chapter, however, illustrates that ring-chlorinated aromatic acids may constitute a more important class of by-products from the chlorination of humic materials under drinking water treatment conditions than previously recognized.

Examples of sample peak mass spectra and the structural formulas tentatively assigned to these spectra are presented (Figure 2). The number of isomers of each structure, as indicated by other peaks having nearly identical mass spectra, are also noted. The mass spectra of the standards used to make the structural assignements are shown (Figure 3). The tentative identification of the peak having the spectrum shown in Figure 2b was initially based solely on its match with the standard spectrum found in the EPA/NIH Mass Sepectral Data Base (Figure 3a). The general fragmenta-

tion pattern and the major m/z peaks, except for the m/z 201 ion, matched very well. Other chromatographic peaks were found with spectra containing similar fragmentation patterns (Figure 2). Calculating the probable masses of the molecular ion and major fragment ion for different combinations of chloro and methyl carboxylate functional groups added to the basic methoxybenzene structure (Table III) provided likely explanations for the spectral data in Figure 2, and the tentative identifications were assigned on that basis. Later, a standard of 5-chloro-2-methoxybenzoic acid, methyl ester, was analyzed under the same conditions as the samples (Figure 3b). The spectral comparison with Figure 2a as well as the excellent RRT comparison (1.020 for the standard compared to 1.022 for the Figure 2a peak) provided further evidence that the tentative structural assignments for the sample peaks had been correct. Although the apparent loss of a neutral mass 33 fragment from the molecular ion, resulting in the m/z 167 peak (Figure 3b), has not been explained structurally, the resulting ion cluster matches well with the spectra of Figure 2.

Although many of the compounds not containing chlorine (Tables I and II) were found in both the chlorinated sample and nonchlorinated controls, the larger areas for many peaks found in the chlorinated samples, particularly the higher molecular weight, later eluting compounds, indicate that these types of compounds are formed during chlorination. This observation is not surprising because chlorine treatment is mainly an oxidative process, and other oxidative processes occur naturally. All of the chlorine containing compounds were definitely by-products of chlorination and were virtually absent for the controls.

Few differences in the types of compounds formed from the chlorination of the different sources of humic acids were observed. Although the Black Lake humic acid produced relatively fewer chlorine containing unknowns (Table II) than the other sources, none of the humic sources produced groups or classes of by-products that were unique to that source. Although some unknowns were detected in only one of the four chlorinated samples, evidence indicating that any one source produced a particular group or series of unknown by-products was not found. The chlorinated Aldrich, Fluka, Black Lake, and Florida lake humic acid extracts respectively included 6, 4, 6, and 10 chlorine containing unknowns and 12, 8, 6 and 4 non-chlorine containing unknowns that were unique to each source. Compounds that were found in the solvent blanks, or that were otherwise suspected of being method artifacts have not been included in the tables. Many compounds that were found at approximately equal concentrations in both chlorinated and nonchlorinated samples were also omitted from the tables. These included alkanes, alkyl substituted benzenes, phthalic acid esters other than methyl esters, and 8 unknowns.

Several additional experiments were included in this study to determine the recoveries and reproducibility of the adsorption/extraction methodologies and to investigate alternative procedures. Because breakthrough studies showed poor removal of TOX and THMs, a chlorinated Aldrich humic acid solution was passed through three XAD-8 resin columns in series in an attempt to determine, by separate extraction and analysis of the columns, which types of compounds were more readily adsorbed. Although hindered by the lack of quantitative precision (discussed below), the data generally showed that adsorption efficiency increased with increasing

molecular weight. Also, in the higher molecular weight range, the initial concentration of the individual compounds greatly affected recovery. For example, certain compounds at high initial concentrations were found at nearly equal levels on all three columns. Other compounds of similar structure, but at low initial concentrations, were found only on the first column. These findings indicate that adsorption capacity as well as adsorption efficiency affected recoveries of many compounds.

An effort to increase the recovery was made by replacing the XAD-8 resin with granular activated carbon (GAC). Figure 4 shows the increased removals of both TOX and THMs by the GAC column, and the peak areas for many of the individual compounds were similarly affected. Notable increases were observed for the chloro- and non-chloro mono- and dibasic aliphatic acids, particularly in the low molecular weight range, as well as for many of the compounds that have not been attributed to chlorination. On the other hand, significant decreases were observed in the recoveries of many of the aromatic compounds, especially in the ring-chlorinated compounds that were of special interest in this study. It is likely that this was because of poor extraction from the GAC rather than poor initial adsorption.

Finally, to evaluate the reproducibility of the methodology, the Aldrich humic acid run was repeated under conditions duplicating those of the first run. For each of 50 compounds that were found in both concentrated extracts of the chlorinated sample, the ratio of the larger area count response to the smaller was calculated after adjusting for the internal standard response. Approximately 54% of the area count pairs were reproducible to a factor of two and 82% to a factor of three (Figure 5).

This level of precision was not sufficient to make all the desired quantitative evaluations of the data and needs to be improved. The low and variable recoveries from the resin by the adsorption and extraction procedures were probably the chief causes for the poor reproducibility.

SUMMARY AND FUTURE CONSIDERATIONS

Most of the compounds and compound groups tentatively identified in this work on chlorination of humic substances at low concentrations have been previously found by others in work that was conducted at high concentrations. This supports the validity of extrapolating high concentration work to predict by-products in drinking water treatment applications. Further research will be required to determine the significance of the tentative identification of numerous ring-chlorinated aromatic acid methyl esters, which had previously been reported by only one investigator.

No major differences were found in the types of compounds produced with the different sources of humic substances used in this study. This consistency is important because the composition of humic materials in a water supply can vary greatly from one geographic area to another, or even from one season to another, and research in this field would be much more complicated if different by-products were produced from different humic sources. This consistency also lends credibility to the health effects studies and other research that has been conducted using commerical sources of humic acid as models.

Finally, although this study demonstrated the practicality of using the described methodology for concentrating and identifying specific compounds from water samples at low concentrations, many improvements, particularly in the areas of recovery and quantitation, are needed. In

future work, a known quantity of a surrogate compound will be added to the original water sample to monitor the recovery of the overall procedure; the internal standard used for quantitative purposes will continue to be added just prior to analysis. Deuterated benzoic acid will be used as a surrogate compound because it fulfills two important requirements; i.e., it mimics the adsorption and extraction characteristics of many of the acidic and aromatic compounds of interest, and it can be easily distinguished from the natural compounds by mass spectral analysis. Also, to improve the total recovery, a GAC column will be added following the XAD-8 resin column. The resin column will be retained to adsorb the aromatic compounds which were poorly recovered in the trial using the GAC column alone. Additionally, the columns will be inverted for the extraction step to avoid passing the compounds that are adsorbed on the resin through the GAC during extraction. These modifications are expected to improve the recovery and provide a reliable means of monitoring the recovery, which should generate more precise quantitative measurements.

Figure 1. Computer reconstructed chromatograms of concentrated extracts from nonchlorinated (a) and chlorinated (b) Fluka humic acid solution. GC conditons: 2.0 uL splitless injection at 35°C; programmed at 4°C/min to 240°C after 5 min. Mass range scanned from m/z 35 to 435 every 2 sec.

Figure 2. Mass spectra and tentatively assigned structures of chromatographic peaks from the concentrated extracts of chlorinated Aldrich humic acid.

Figure 3. Mass spectra of standard compounds used to make the tentative structural assignments in Figure 2. a) 3,5-dichloro-2-methoxybenzoic acid, methyl ester, from the EPA/NIH Masss Sepctral Data Base; b) 5-chloro-2-methoxybenzoic acid, methyl ester, standard run under the same GC/MS conditions as the samples.

Figure 4. Adsorption of total organic halogen and trihalomethane from chlorinated Aldrich humic acid solution on 50 cm of XAD-8 resin compared to 25 cm of granular activated carbon.

Figure 5. Recovery of individual compounds from duplicate analyses of chlorinated Aldrich humic acid samples.

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TABLE Ia. TENTATIVELY IDENTIFIED OR CHARACTERIZED COMPOUNDS NOT CONTAINING CHLORINE FOUND IN EITHER THE CHLORINATED SAMPLES OR NONCHLORINATED CONTROLS

Compound	RRT[a]	Humic Acid Sources (Area counts x 1000)							
		Aldrich		Fluka		Black Lake, NC		Florida Lake Water	
		S[b]	C[c]	S	C	S	C	S	C
Aliphatic Acid, methyl esters									
2-Hydroxypropanoic	0.249	-	-	-	-	39	41	3	4
Hexanoic	0.436	1	1	1	-	3	1	1	-
Heptanoic	0.552	2	-	2	-	3	1	1	-
Octanoic	0.662	4	2	3	1	6	1	1	1
Nonanoic	0.765	3	3	2	-	3	1	-	-
Decanoic	0.863	4	-	2	-	4	1	1	-
Dodecanoic	1.041	5	4	6	2	10	1	2	1
Compound #265	1.097	-	-	-	-	1	-	-	-
Compound #123	1.124	2	-	2	-	-	-	-	-
Compound #126	1.134	1	-	1	-	-	-	-	-
Compound #132	1.175	1	-	-	-	-	-	-	-
Tetradecanoic	1.203	10	7	11	1	17	4	4	2
Compound #139	1.213	1	-	1	-	-	-	-	-
Compound #227	1.232	-	-	-	-	-	1	-	-
Compound #145	1.258	1	1	-	-	4	-	2	-
Compound #204	1.285	-	-	-	-	5	2	2	1
Hexadecanoic	1.355	52	32	14	4	70	28	15	-
Compound #230	1.432	-	-	-	-	-	1	-	-
Compound #377	1.482	-	-	-	1	-	-	-	-
Octadecanoic	1.513	10	-	-	-	-	21	-	-
Compound #206	1.533	-	-	-	-	28	-	-	-
Ethanedioic	0.331	-	-	13	-	7	6	6	3
Propanedioic	0.445	2	1	2	-	1	-	1	1
Butanedioic[d]	0.556	-	-	14	12	2	1	1	-
Octanedioic	0.965	1	-	1	-	-	-	-	-
Nonanedioic	1.052	7	1	2	-	1	-	-	-
Aromatic Acid, methyl esters									
Benzoic[d]	0.628	11	-	18	4	10	-	28	16
Benzenedicarboxylic	0.982	20	5	9	7	10	6	15	3
Benzenedicarboxylic	1.018	9	2	7	-	3	-	6	1
Benzenedicarboxylic	1.029	8	-	9	-	4	-	17	-
Benzenetricarboxylic	1.294	44	5	25	-	18	-	10	-
Benzenetricarboxylic	1.340	10	-	6	-	4	-	5	-
Benzenetricarboxylic	1.454	2	-	-	-	1	-	-	-
Benzenetetracarboxylic	1.534	-	-	6	-	-	-	-	-
3-Methoxybenzoic	0.909	3	-	1	-	2	-	2	-
Methylbenzenedicarboxylic	1.078	4	-	1	-	-	-	-	-
Methylbenzenedicarboxylic	1.103	1	-	1	-	-	-	-	-
Methylfurancarboxylic	0.601	2	-	1	-	2	-	1	-
Methylfurandicarboxylic	0.959	32	-	14	-	9	-	11	-

[a]Retention time relative to internal standard.
[b]Sample
[c]Control
[d]Identification confirmed by mass spectrum and retention time of an authentic standard.

TABLE Ib. TENTATIVELY IDENTIFIED OR CHARACTERIZED CHLORINE CONTAINING COMPOUNDS FOUND IN EITHER THE CHLORINATED SAMPLES OR NONCHLORINATED CONTROLS

Compound	RRT[a]	Humic Acid Sources (Area Counts x 1000)							
		Aldrich		Fluka		Black Lake, NC		Florida Lake Water	
		S[b]	C[c]	S	C	S	C	S	C
Aliphatic Acid, methyl esters									
Chloroacetic[d]	0.256	1	-	1	-	6	-	2	-
Dichloroacetic[d]	0.343	18	-	49	-	83	5	46	-
2,2-Dichloropropanoic	0.364	2	-	2	-	2	-	7	-
Trichloroacetic[d]	0.428	32	-	64	-	-	-	64	-
Bromochloroacetic	0.434	-	-	-	-	-	-	1	-
3,3-Dichloropropenoic	0.451	13	-	-	-	-	-	11	-
Dichloroacetic acid, ethyl ester	0.420	1	-	-	-	-	-	-	-
Trichloroacetic acid, ethyl ester	0.504	1	-	-	-	-	-	-	-
Trichloroacetic acid	0.859	-	-	-	-	1	-	20	-
Aromatic Acid, methyl esters									
5-Chloro-2-methoxybenzoic[d]	1.022	8	-	2	-	1	-	-	-
Dichloromethoxybenzoic	1.060	20	-	11	-	19	-	3	-
Dichloromethoxybenzoic	1.070	1	-	1	-	-	-	-	-
Chloromethoxybenzenedicarboxylic	1.231	9	-	-	-	2	-	1	-
Chloromethoxybenzenedicarboxylic	1.240	4	-	1	-	-	-	-	-
Chloromethoxybenzenedicarboxylic	1.267	63	-	21	-	8	-	11	-
Dichloromethoxybenzenedicarboxylic	1.291	13	-	2	-	7	-	-	-
Chloromethoxybenzenedicarboxylic	1.314	17	-	5	-	-	-	-	-
Dichloromethoxybenzenedicarboxylic	1.331	41	-	7	-	11	-	2	-
Chloromethoxybenzenetricarboxylic	1.466	24	-	1	-	6	-	-	-
Chloromethoxybenzenetricarboxylic	1.534	16	-	4	-	4	-	-	-

[a] Retention time relative to the internal standard.
[b] Sample
[c] Control
[d] Indentification confirmed by mass spectrum and retention time of an authentic standard.

TABLE II. UNIDENTIFIED COMPOUNDS (UNKNOWNS) FOUND IN MORE THAN ONE OF EITHER THE CHLORINATED SAMPLES OR UNCHLORINATED CONTROLS

Compound ID No.	RRT[a]	Humic Acid Sources (Area Counts x 1000)							
		Aldrich		Fluka		Black Lake, NC		Florida Lake Water	
		S[b]	C[c]	S	C	S	C	S	C
Compounds Not Containing Chlorine									
255	.284	–	–	–	–	3	1	2	3
25	.330	2	1	–	–	2	–	–	–
207	.348	1	–	–	–	4	–	–	–
261	.781	–	–	–	–	3	–	1	–
174	.795	1	2	3	–	–	–	–	–
105	1.015	27	4	45	–	–	–	–	–
110	1.031	9	2	11	–	–	–	2	–
216	1.097	2	–	5	–	–	–	–	–
129	1.160	2	–	4	–	1	–	–	–
226	1.191	–	–	1	2	3	1	13	15
140	1.223	2	1	6	–	–	–	–	–
148	1.280	14	–	28	–	–	–	–	–
228	1.292	–	–	1	–	–	–	1	–
162	1.410	2	–	–	–	1	–	–	–
165	1.436	–	–	4	–	1	–	–	–
Compounds Containing Chlorine									
208	.415	2	–	2	–	–	–	3	–
209	.490	10	–	12	–	–	–	16	–
210	.647	12	–	9	–	–	–	19	–
279	.665	–	–	2	–	–	–	7	–
65	.685	2	–	2	–	–	–	2	–
71	.718	6	–	10	–	7	–	11	–
280	.726	–	–	2	–	–	–	2	–
281	.730	–	–	2	–	–	–	2	–
283	.759	–	–	1	–	–	–	4	–
83	.798	11	–	11	–	1	–	7	–
85	.812	1	–	2	–	1	–	1	–
87	.833	2	–	2	–	–	–	4	–
302	.870	–	–	1	–	–	–	4	–
93	.893	3	-	9	–	1	–	2	–
94	.902	8	–	10	–	2	–	16	–
97	.945	2	–	1	–	–	–	–	–
287	.953	–	–	2	–	–	–	1	–
288	.996	–	–	2	–	–	–	6	–
289	1.016	–	–	4	–	–	–	7	–
114	1.055	4	–	3	–	–	–	7	–
290	1.148	–	–	–	–	6	–	5	–
127	1.150	1	–	–	–	–	–	1	–
135	1.193	3	–	4	2	–	–	–	–
136	1.199	1	–	4	–	–	–	–	–
138	1.210	13	–	5	–	3	–	24	–
143	1.248	17	–	54	5	3	–	7	–

[a]Retention time relative to the internal standard.
[b]Sample
[c]Control

TABLE III. EXPECTED MASS PEAKS FROM DIFFERENT COMBINATIONS OF CHLORINE AND METHYL CARBOXYLATE FUNCTIONAL GROUPS ON METHOXYBENZNE

(m/z of molecular ion / m/z of principal fragment ion)

		Number of Methyl Carboxylate Groups		
		1	2	3
Number of	1	200/169	258/227	316/285
Chlorine	2	234/203	292/261	350/329
Atoms	3	268/237	326/295	

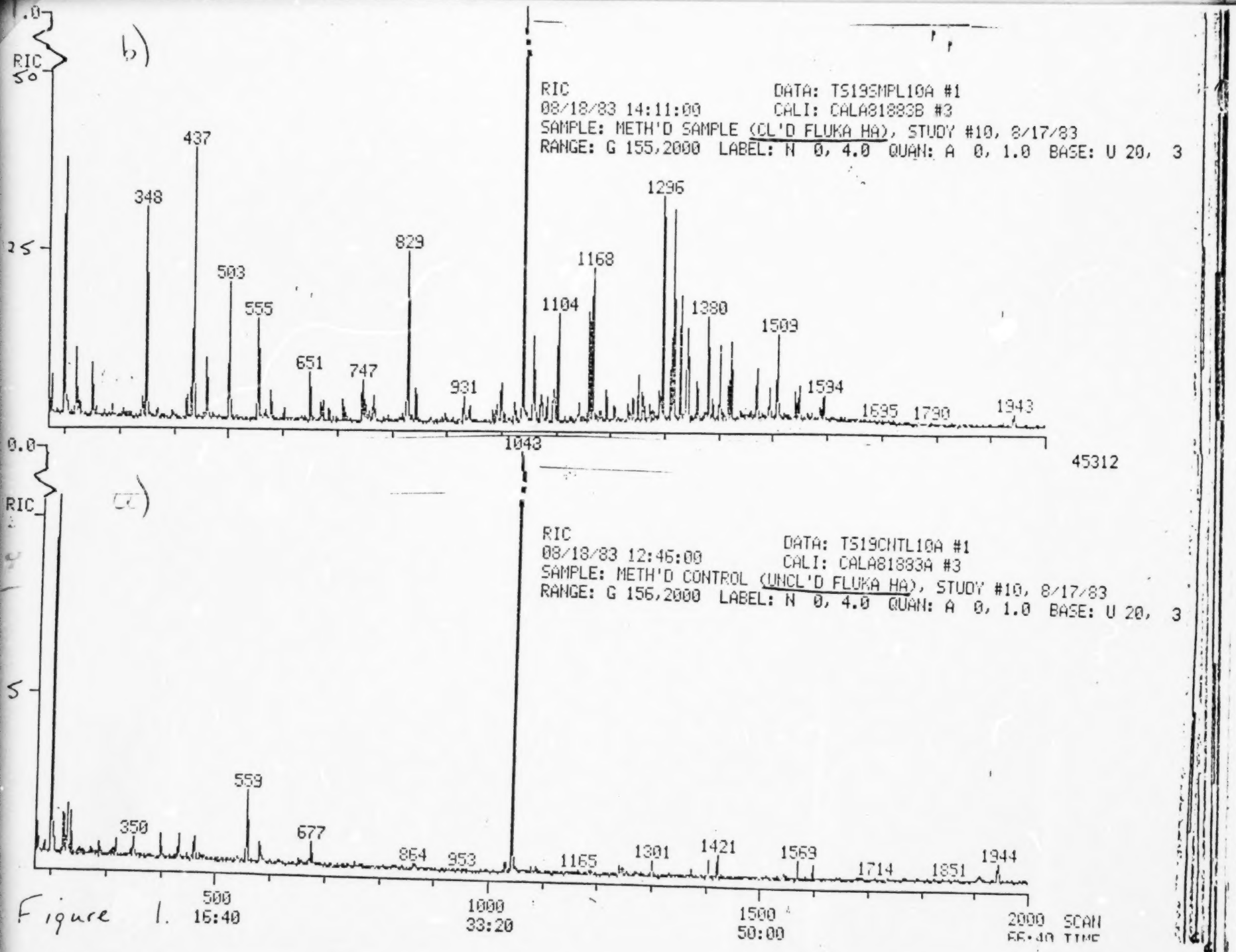
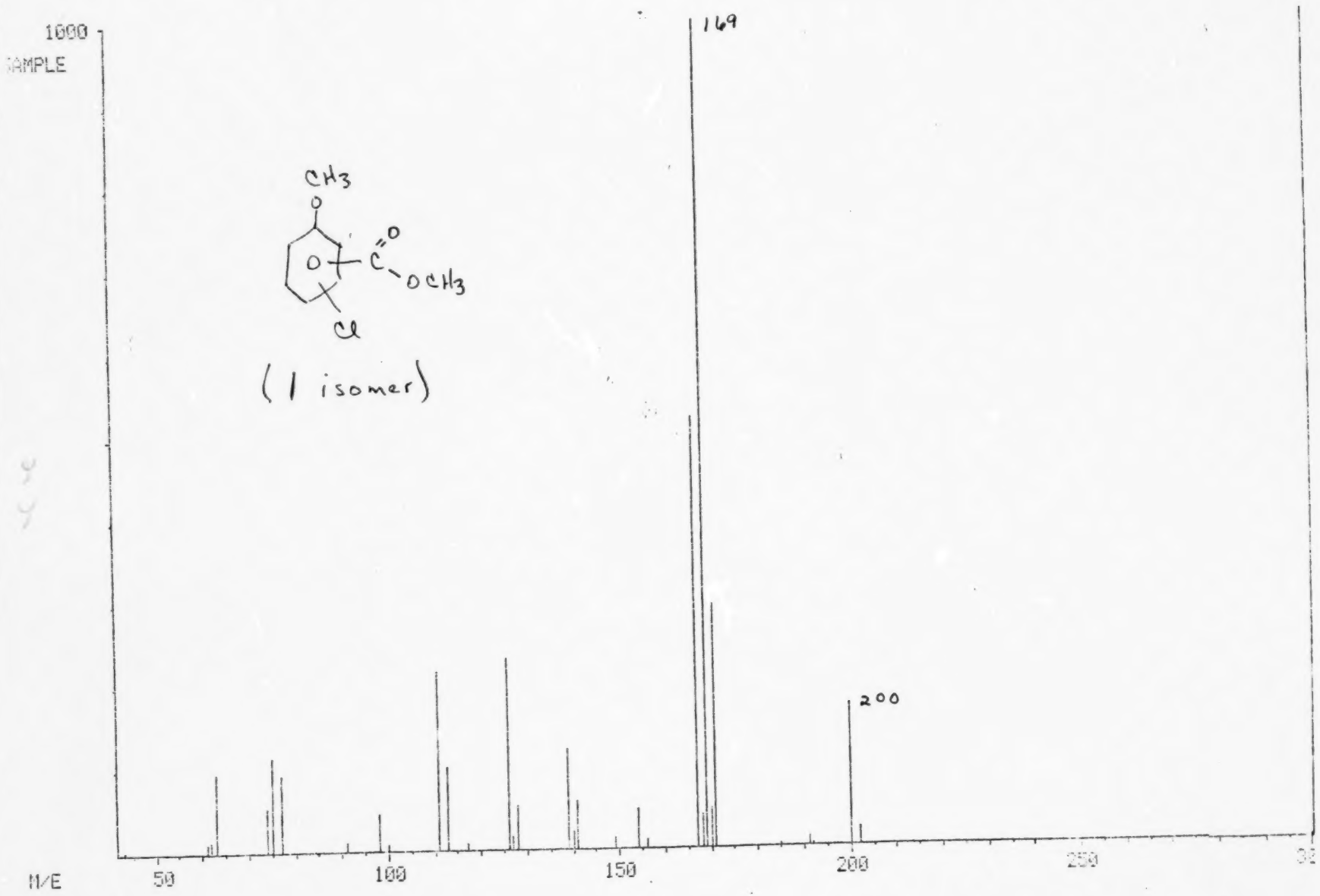

b)
RIC
50
25
0.0
RIC
DATA: TS19SMPL10A #1
08/18/83 14:11:00
CALI: CALA81883B #3
SAMPLE: METH'D SAMPLE (CL'D FLUKA HA), STUDY #10, 8/17/83
RANGE: G 155,2000 LABEL: N 0, 4.0 QUAN: A 0, 1.0 BASE: U 20, 3
437
348
503
555
829
651
747
931
1104
1168
1296
1380
1509
1594
1635
1790
1943
1043
45312
c)
RIC
5
0.0
RIC
DATA: TS19CNTL10A #1
08/18/83 12:46:00
CALI: CALA81883A #3
SAMPLE: METH'D CONTROL (UNCL'D FLUKA HA), STUDY #10, 8/17/83
RANGE: G 156,2000 LABEL: N 0, 4.0 QUAN: A 0, 1.0 BASE: U 20, 3
559
350
677
854
953
1165
1301
1421
1569
1714
1851
1944
500
16:40
1000
33:20
1500
50:00
2000 SCAN
TIME

Figure 1.

LIBRARY SEARCH Aldrich peak # 107 DATA: USER DEFINED BASE M/E:169



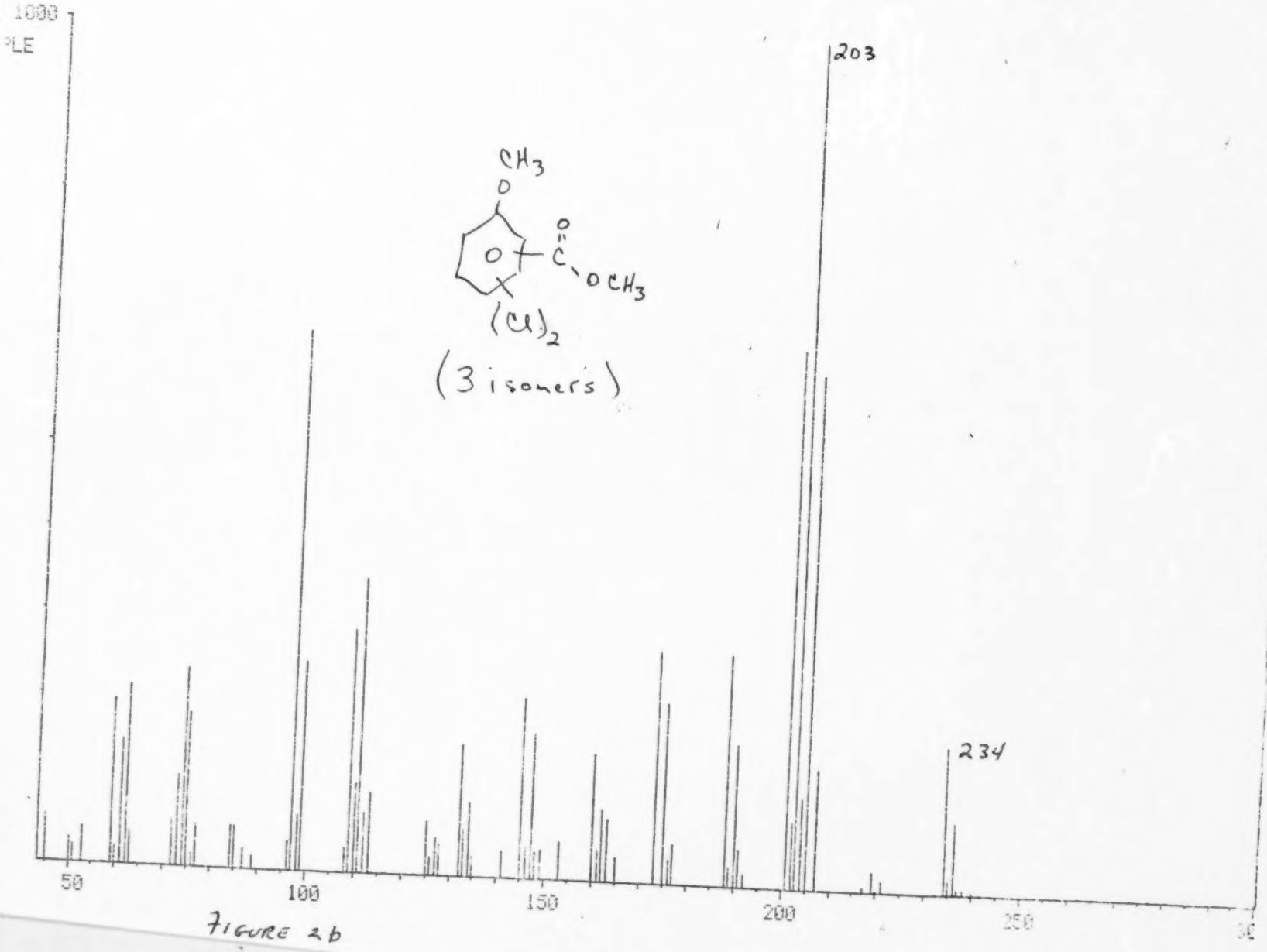
(1 isomer)

Figure 2a.

LIBRARY SEARCH Aldrich peak #115

DATA: USER DEFINED

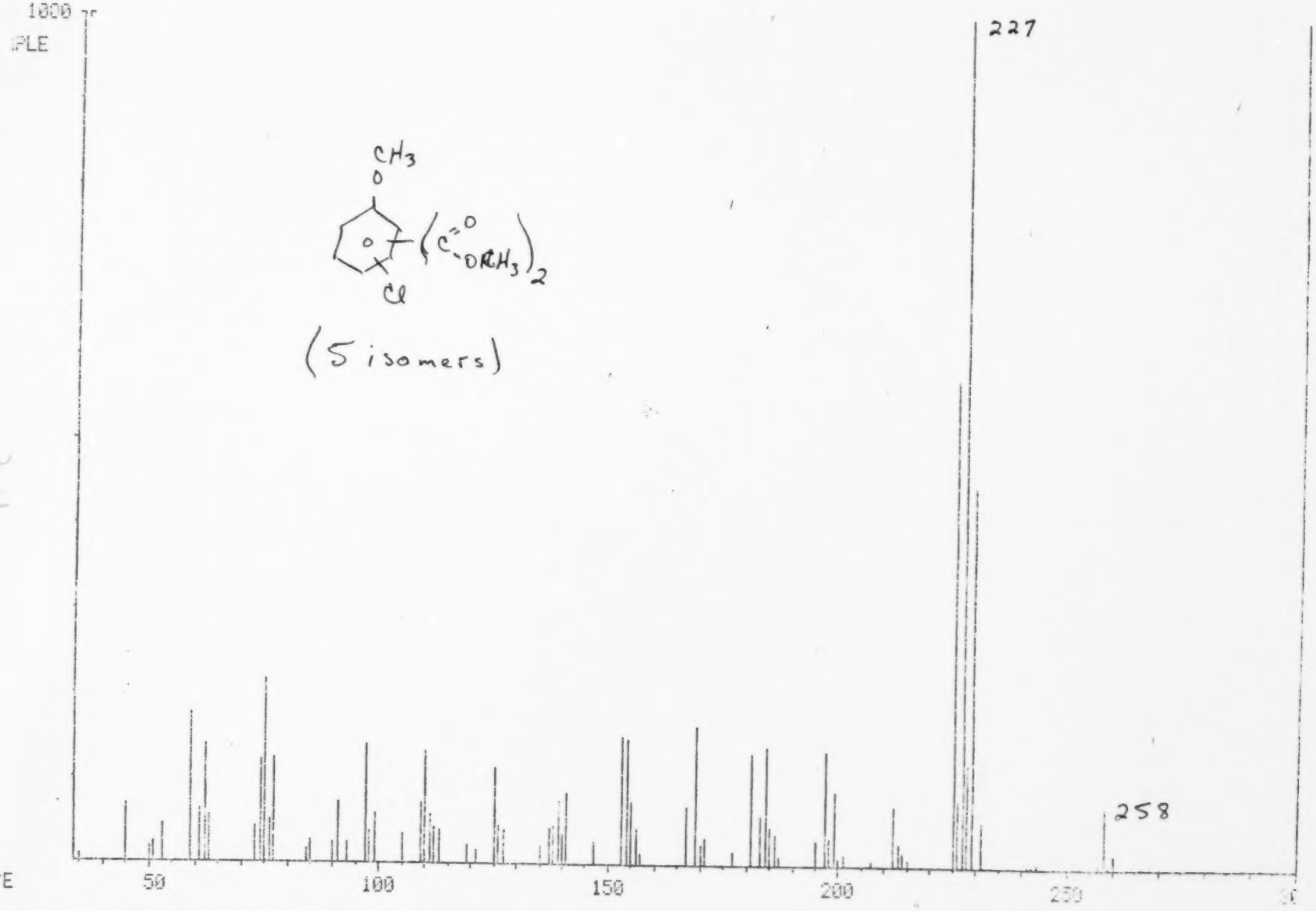
BASE M/E:203



(3 isomers)

FIGURE 2b

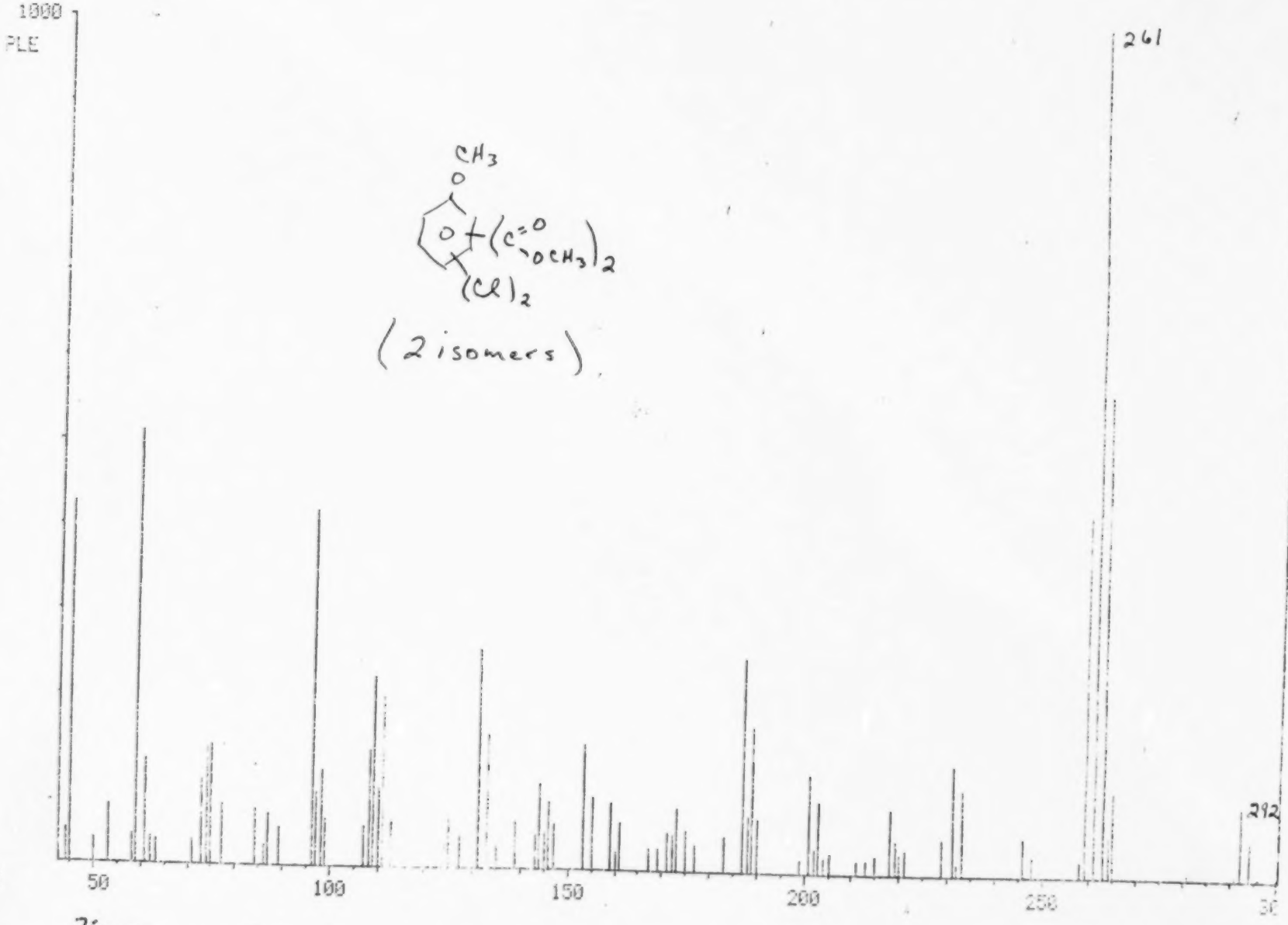
LIBRARY SEARCH Aldrich peak #157 DATA: USER DEFINED BASE M/E:227



(5 isomers)

FIGURE 2c

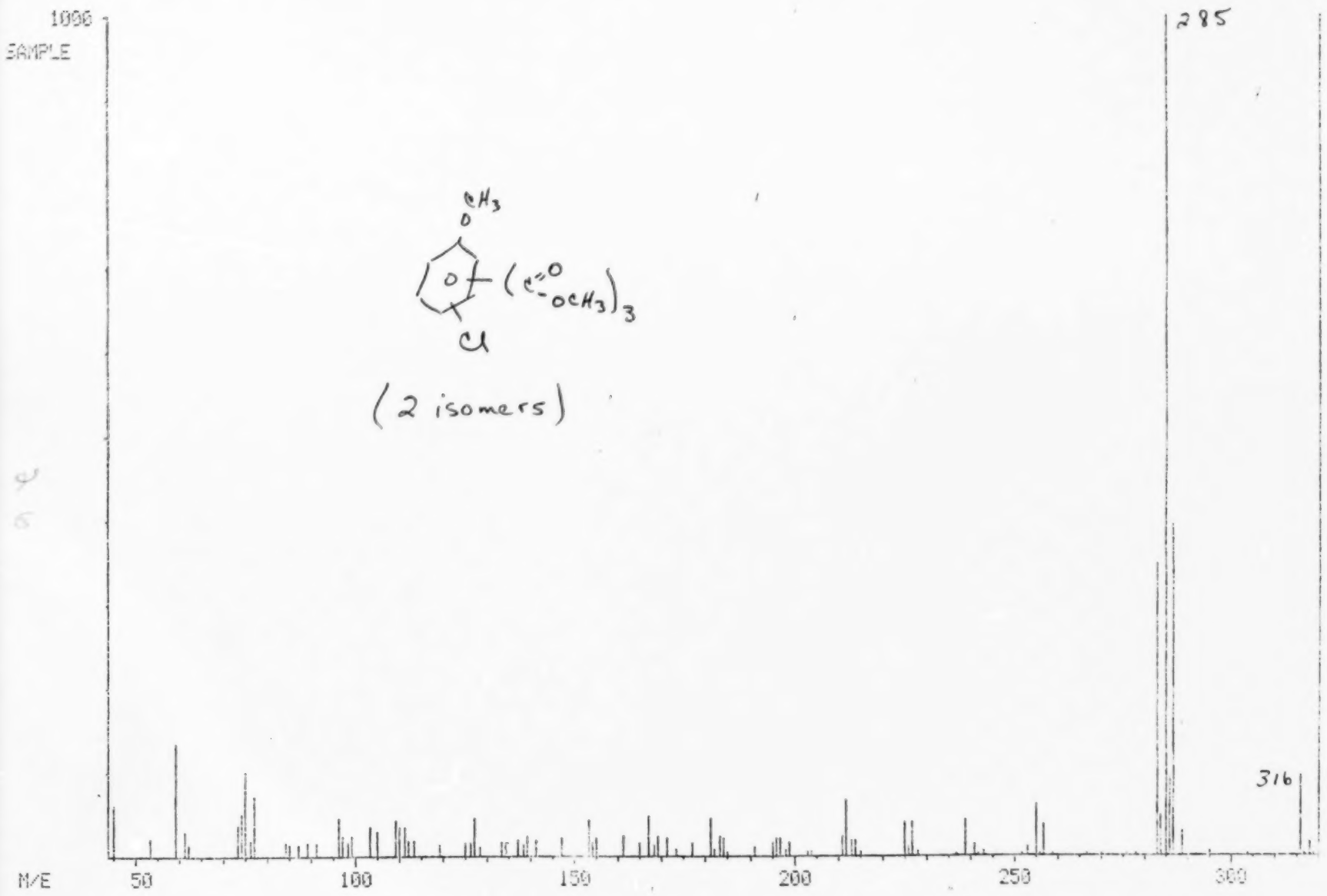
LIBRARY SEARCH Aldrich Peak #153 DATA: USER DEFINED BASE M/E:261



(2 isomers)

Figure 2d

LIBRARY SEARCH Aldrich peak #171 DATA: USER DEFINED BASE M/E:285



(2 isomers)

Figure 2e.

LIBRARY SEARCH NB Library DATA: USER DEFINED BASE

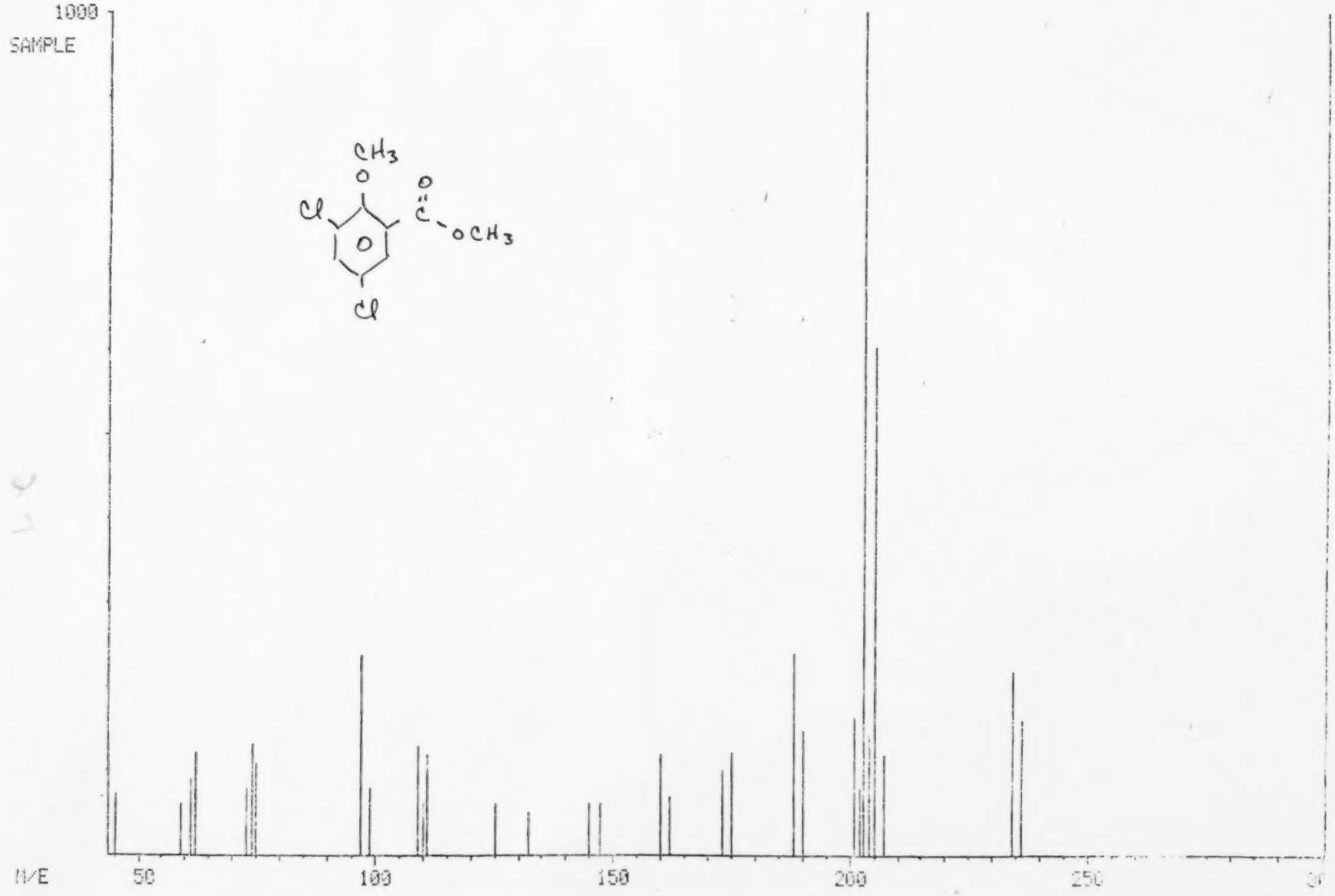


Figure 3a.

LIBRARY SEARCH Std. 5-Chloro-2-methoxybenzoic acid, ME DATA: USER DEFINED BASE M/E:169

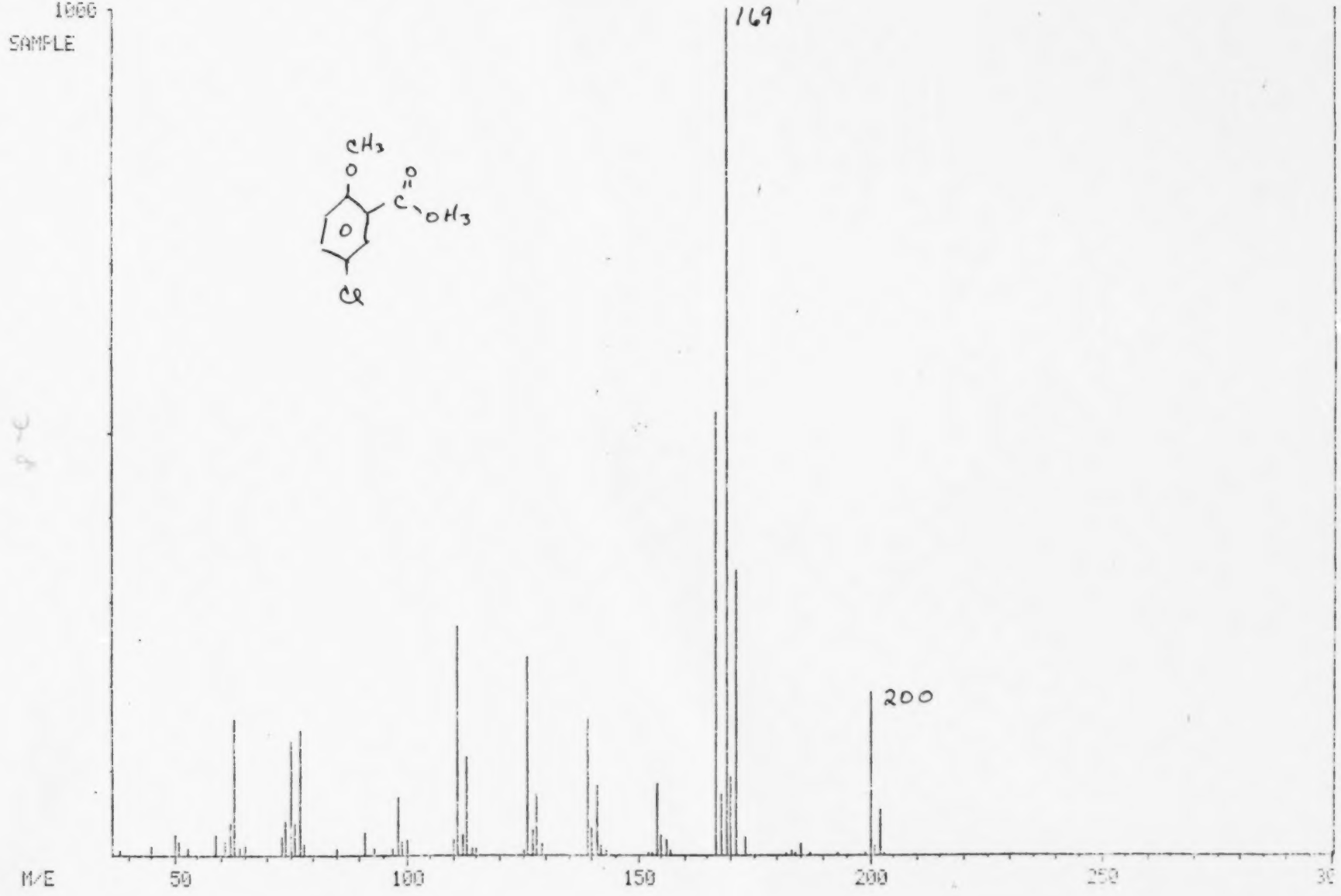


Figure 3b.

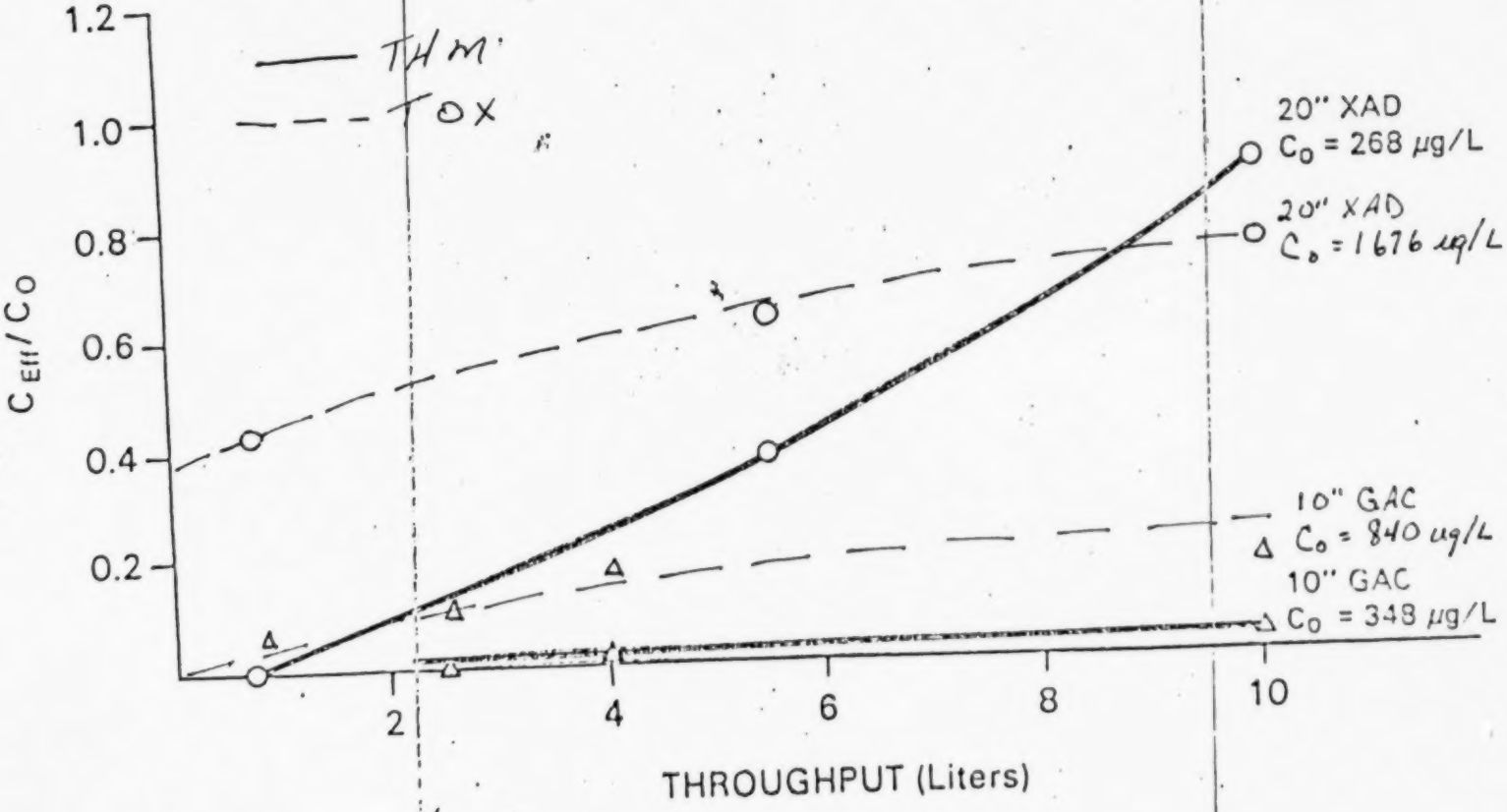


Figure 4

Total Organic Halogen and Trihalomethane Breakthrough

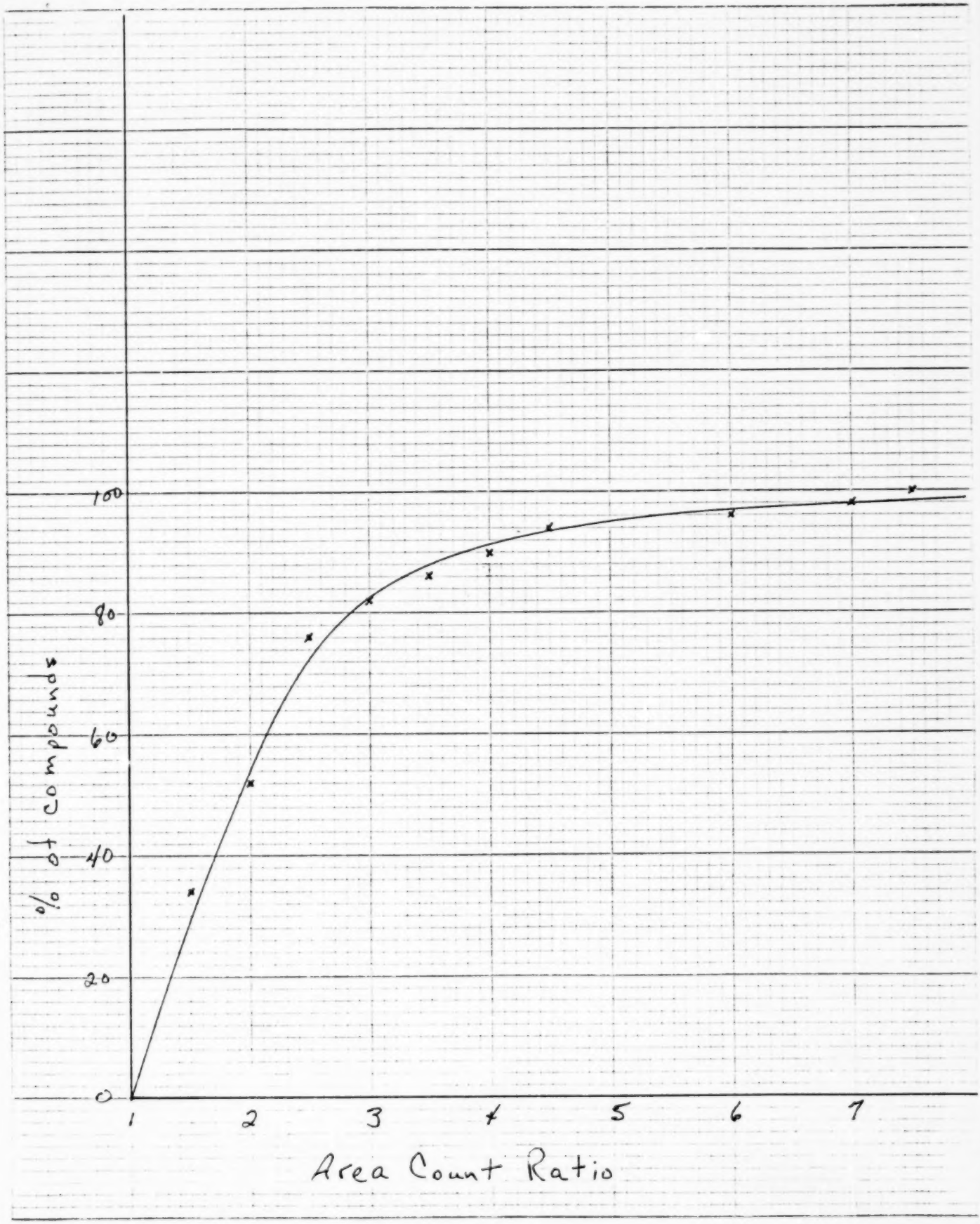


Figure 5.